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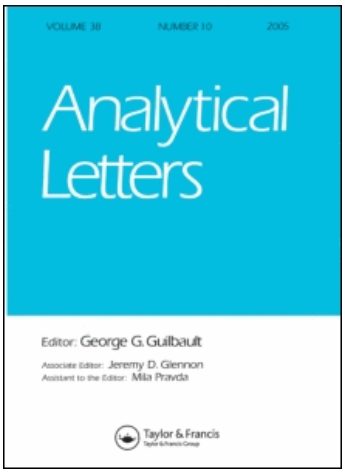

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SENSORS

Synthesis and Applications of a New Polysiloxane-Immobilized Macrocyclic Ligand System

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Abstract: Insoluble porous solid, macrocyclic 22-membered ring, 1-oxa-6,9,12,15,18-pentaaza-2,22-disilacyclododocosane polysiloxane ligand system has been prepared by the reaction of a macro-silane agent with tetraethylorthosilicate. The macro-silane agent was prepared by the reaction of imino-bis(N-2-aminoethylacetamide) ligand with 3-iodopropyltrimethoxysilane in 1:3 molar ratio. The new prepared polysiloxane system exhibits variable potentials for the extraction of metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) from aqueous solutions. The ligand system shows high capacity to extract silver, lead, and mercury. Chemisorption of the metal ions by the ligand system at the optimum conditions was found in the order $Ag^{+} > Pb^{2+} > Hg^{2+} > Cu^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+} > Cd^{2+} > Zn^{2+}$.

Keywords: Chelating ligands, extraction of metal ions, immobilized-polysiloxane ligand systems, macrocycle, metal uptake

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INTRODUCTION

Preconcentration and separation of dissolved trace elements by a chemically modified solid supports have been studied intensively in recent years (Castro et al. 2004; Toledo, Gushikem, and Castro 2000; Navarro 2001; Moawed, Zaid, and El-Shahat 2005; Prado, Arakaki, and Airoldi 2001; Garg et al. 1999, 2002; Filho et al. 1996; Som-Aum et al. 2007; Pochinok et al. 2007; Campos and Gushikem 1997; Spinacé, Cardoso, and Schuchardt 1997; Preetha and Prasada Rao 2006). The polysiloxane-immobilized ligand systems have become particularly attractive solid supports because of their mechanical, thermal, and chemical stability. The polysiloxane-immobilized ligand systems have become of great importance in science and industry, because of their widespread applications. These immobilized ligand systems can be synthesized primarily by the sol-gel process (Khatib and Parish 1989; Ahmed and Parish 1993; El-Ashgar and El-Nahhal 2005; Parish, Habibi, and Mohammadi 1989; El-Nahhal, Zaggout, and El-Ashgar 2000). The sol-gel method includes hydrolysis and polycondensation of $Si(OEt)_4$ and the appropriate silane coupling agent. Further chemical modification of functionalized polysiloxane-immobilized ligand systems have been used to produce new polysiloxane derivatives (El-Nahhal and El-Ashgar 2007; El-Kurd, El-Nahhal, and El-Ashgar 2005; Saadeh et al. 2005; El-Ashgar et al. 2006). The incorporation of chelating groups onto polysiloxanes is finding its way into an increasing number of applications in areas such as extraction of metal cations from organic and aqueous media (Khatib and Parish 1989; Ahmed and Parish 1993; El-Ashgar and El-Nahhal 2005; Parish, Habibi, and Mohammadi 1989; El-Nahhal, Zaggout, and El-Ashgar 2000; El-Nahhal and El-Ashgar 2007; El-Kurd, El-Nahhal, and El-Ashgar 2005; Saadeh et al. 2005; El-Ashgar et al. 2006), use as stationary phases in liquid chromatography (El-Ashgar and El-Nahhal 2005, 2006; El-Nasser and Parish 1999; Trojer et al. 2005), and for the catalysis of reactions (Parish, Habibi, and Mohammadi 1989; Cermak et al. 1996; Klonkowski, Widernik, and Grobelna 2001). Such materials have many advantages over organic resins, because of their high thermal, hydrolytic, and mechanical stability, in addition to lack of swelling in solvents (Elfferich 1962; Lier 1979). Many techniques have recently been applied to characterize their chemical structures (Yang et al. 1997a, 1997b; Yang, El-Nahhal, and Maciel 1996; El-Nahhal et al. 1996, 2003; Jovanovic et al. 1998). In this work, a new functionalized macrocyclic ligand system was made to investigate its metal uptake capacity toward some metal ions (including Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) in aqueous solutions.

EXPERIMENTAL

Reagents and Materials

Tetraethylorthosilicate, 3-chloropropyltrimethoxysilane, ethylenediamine, and iminodiacetic acid were purchased from Merck and used as received. Acetone, diethyl ether, and methanol (spectroscopic grade) were used as received. Metal ion solutions of the appropriate concentrations were prepared by dissolving the metal chlorides (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}) and metal nitrates (Ag^{+}, Hg^{2+}, and Pb^{2+}) in distilled water (all of them were analytical grade salts). Different pH ranges (3.5–6) were controlled using acetic acid/sodium acetate buffer solutions.

General Techniques

Analysis for carbon, hydrogen, and nitrogen were carried out using an elemental analyzer EA 1110-CHNS CE instrument. The infrared spectra for the materials were recorded on a Perkin-Elmer FTIR spectrometer using KBr disk in the range 4000 to 400 cm^{-1}. All pH measurements were obtained using an HM-40 V pH meter.

Methods of Preparation

Preparation of 3-Iodopropyltrimethoxysilane (L-I)

The 3-iodopropyltrimethoxysilane was prepared as previously described (Ahmed and Parish 1993), where 3-chloropropyltrimethoxysilane (19.87 g, 0.10 mol) was added dropwise to a solution of sodium iodide (15 g, 0.10 mol) in 100 mL of dry acetone with stirring, at room temperature. The mixture was refluxed at 70°C for 48 h. White solid of NaCl was filtered off, and the solvent was removed under reduced pressure at 60°C. The residue was extracted four times with 100 mL of diethyl ether using a separatory funnel. The diethyl ether was removed at 35°C under reduced pressure producing a light yellow oily product.

Preparation of Diethyliminodiacetae (DEIDA)

This compound was prepared as previously reported (El-Kurd, El-Nahhal, and El-Ashgar 2005; El-Nasser and Parish 2006) by adding iminodiacetic acid (30.0 g, 0.4 mol) to 300 ml of absolute ethanol with stirring, to which thionyl chloride (93.86 g, 0.8 mol) was added dropwise.

The reaction mixture was stirred and refluxed at 80°C until all the iminodiacetic acid was dissolved. The reaction was allowed to proceed under reflux for 5 h. The mixture was cooled to room temperature, and the excess ethanol and SO_2 were removed by evaporation under vacuum. The residue was dissolved in 100 ml of distilled water, and 150 ml of chloroform were added. Then 33% sodium hydroxide solution was added dropwise with shaking after each addition, so that the diethyliminidiacetate passed into the chloroform, and the pH of the solution was adjusted to around 7. The compound in the aqueous layer was extracted repeatedly with chloroform (4×150 ml). The layer of chloroform was separated and then dried for 2 h over anhydrous $MgSO_4$. The chloroform was removed at reduced pressure, and the residue was dried in vacuum (0.1 torr) for at least 1 h.

Preparation of Imino-bis(N-2-aminoethylacetamide) Ligand (L-IBAEA)

Diethyliminodiacetate (18.9, 0.1 mol) was refluxed with 12.0 g (0.2 mol) of ethylenediamine in 100 ml of ethanol at 70°C for 48 h. Ethanol was removed at reduced pressure, and the residue was dried in vacuum (0.1 torr) for at least 1 h.

Preparation of Macro-Silane Agent (L-Macro)

The imino-bis(N-2-aminoethylacetamide) ligand (10.9 g 0.05 mol) was reacted with 43.5 g (0.15 mol) of 3-idopropyltrimethoxysilane under reflux in the presence of ethanol (50 ml) for 8 h. Ethanol was removed at reduced pressure, and the residue product was dried in vacuum (0.1 torr) for at least 1 h.

Preparation of Polysiloxane Macrocyclic Ligand System (P-Macro)

The macrocyclic ligand system was prepared by adding 5.89 g (0.01 mol) of the macro-silane agent to 6.24 g (0.03 mol) of tetraethylorthosilicate in 20 ml ethanol while stirring, followed by 5.67 g of H_2O. The mixture was left under stirring until gelation occurred (within 1 min). The gel was left for 12 h and then dried at 100°C. The material was crushed, sieved, and washed with successive portions (50 ml) of water, methanol, and diethyl ether. Finally the product was dried for 12 h at 100°C.

Metal Uptake Experiments

One hundred mg of functionalized polysiloxane-immobilized macrocyclic ligand system was shaken with 25 mL of 0.01 M aqueous solution of the

appropriate metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) using 100-mL polyethylene bottles. Determination of the metal ion concentration was carried out by allowing the insoluble complex to settle down, and an appropriate volume of the supernatant was withdrawn using a micropipette, then diluted to the linear range of the calibration curve for each metal. The metal ion uptake was calculated as mg of M^{n+}/g ligand. Metal uptake was examined at different pH values.

Recovery of Metal Ions from Their Ligand Complexes

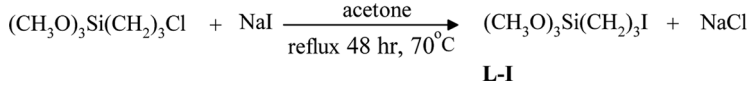
This was carried out by two methods. The first was by treating the metal complexes of the immobilized ligand system with EDTA. A definite amount of the metal-ligand complex (100 mg) was mixed with 35 mL of EDTA (0.1 M) at pH 10 using ammonium buffer. The mixture was left with shaking for 72 h. The metal ion concentration that detached from the solid ligand complex and bound to EDTA was diluted and determined by means of atomic absorption spectroscopy. The second method was achieved by washing the ligand complex with 50 mL of 1.0 M HCl for 30 min.

RESULTS AND DISCUSSION

Preparation of 3-Iodopropyltrimethoxysilane (L-I)

The 3-iodopropyltrimethoxysilne was obtained from the reaction of 3-chloropropyltrimethoxysilane with an excess of sodium iodide using acetone as a solvent under reflux (Scheme 1). The elemental analysis results of the product are given in Table 1.

From the elemental analysis data, it is clear that most of chlorine atoms have been replaced by iodine. The slight decrease of the percentages of C, H, and I from the expected values is obviously due to incomplete replacement of Cl with I.



Scheme 1. Preparation of 3-iodopropyltrimethoxysilne.

Table 1. Elemental analysis data for 3-iodopropyltrimethoxysilane L-I

Element	Expected (%)	Found (%)
C	24.8	23.2
H	5.3	4.6
Cl	0.0	1.5
I	43.8	40.5
C/I	6.0	6.0

Preparation of Diethyliminodiacetate (DEIDA)

The DEIDA was prepared by direct reaction of iminodiacetic acid with absolute ethanol in the presence of thionyl chloride as given in Scheme 2. The elemental analysis is given in Table 2.

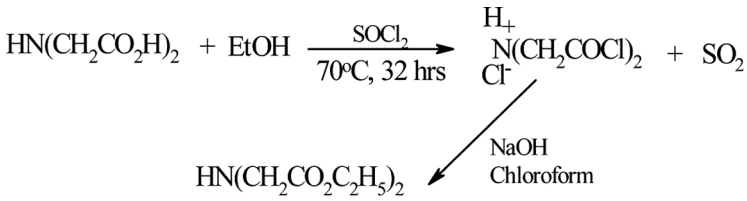
Preparation of Imino-bis(N-2-aminoethylacetamide) Ligand (L-IBAEA)

This ligand was prepared by the reaction of DEIDA with ethylene diamine in ethanol under reflux (Scheme 3). The percentage yield was 94.5%.

Preparation of Polysiloxane-Immobilized Macrocyclic Ligand System (P-IBAEA)

This ligand system was prepared in two steps:

1. Preparation of the macrocyclic iodosilane agent precursor by the reaction of IBAEA with 3-iodopropyltrimethoxysilane (P-I) in 1:3 molar ratio (Scheme 4).
2. Hydrolytic polycondensation of the previous precursor with tetraethylorthosilicate (TEOS) in 1:3 molar ratio (Scheme 4).



Scheme 2. Preparation of Diethyliminodiacetate.

Table 2. Elemental analysis data for diethyliminodiacetate

Element	Expected (%)	Found (%)
C	50.8	51.2
H	8.2	8.3
N	7.30	7.31
C/N	8.00	8.17

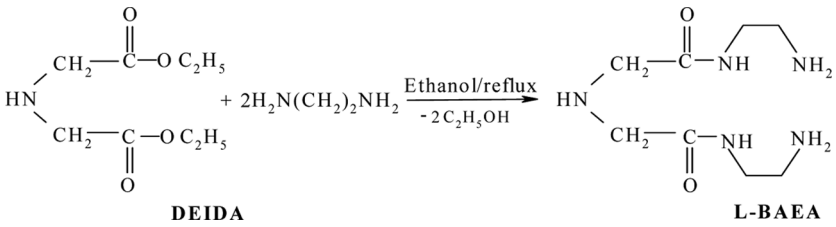
The elemental analysis result of P-macro is given in Table 3. The lower C and N percentages than expected are probably due to incomplete substitution reaction of the iodide. The nitrogen percentage indicates that each gram of P-macro ligand system contains 1.3 mmol of the macrocyclic organofunctionalized group.

The suggested structure of the P-macro is based on the stoichiometry of the reactants in step 2. The found elemental analysis results of P-macro compared with those expected (Table 3) may confirm the proposed structure.

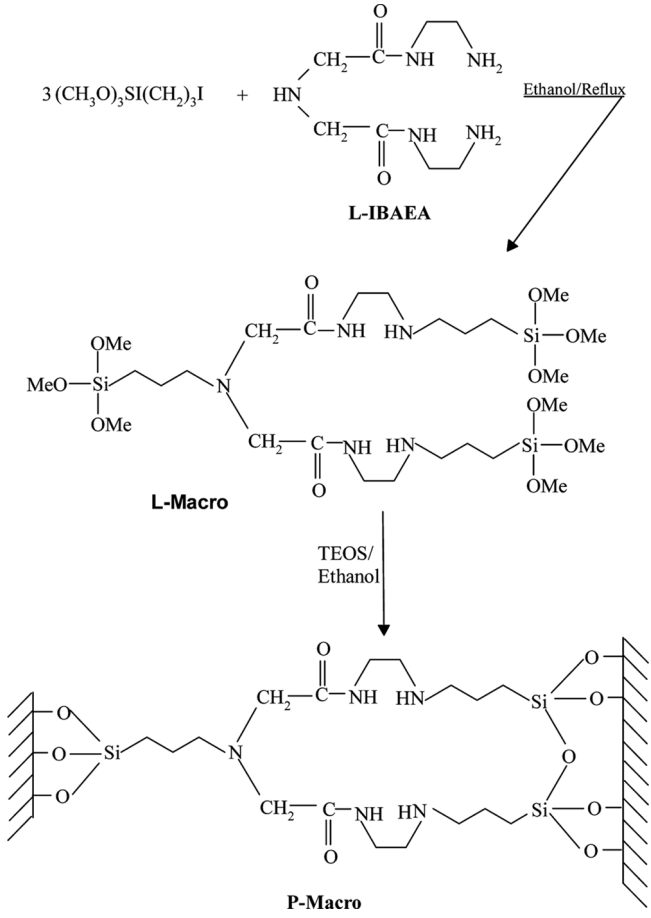
FTIR Spectra

The FTIR spectrum of the DEIDA shows two characteristic bands at 1738 cm^{-1} and 3352 cm^{-1} for ν(C=O) ester and ν(N−H) secondary amine stretching vibrations respectively. The spectrum shows also an absorption band at 1372 cm^{-1}, which belongs to CH_3 bending vibration of the aliphatic ethoxy groups.

The FTIR spectrum of the L-IBAEA shows a characteristic absorption at 1648 cm^{-1} for ν(N–C=O) amide, stretching vibration, and no band for the ester carbonyl ν(C=O) vibration. This confirmed that the reaction between DEIDA and ethylenediamine is complete. The spectrum shows two peaks at 3357 and 3466 cm^{-1}, which are assigned for the ν(N–H) and ν(N−H_2) stretching vibrations. The spectrum also shows a band at 1561 due to δ(N−H) bending vibration.



Scheme 3. Preparation of Imino-bis(*N*-2-aminoethylacetamide).



Scheme 4. Prepartion of Polysiloxane-Immobilized Macrocyclic Ligand System.

Table 3. Elemental analysis for P-macro polysiloxane ligand system

Element	Expected (%)	Found (%)
C	31.7	28.2
H	5.3	4.6
N	10.9	9.2
C/N	40.1	42.7

The FTIR spectrum of the L-IBAEA iodo silane agent (L-macro) shows a characteristic absorption band at 1648 cm^{-1} for ν(N–C=O) amide, stretching vibration. Broad bands are observed at 3452 cm^{-1} and 1077 cm^{-1}, which are assigned to hydrolyzed and condensed silanol groups respectively.

The FTIR spectrum of the P-macro shows three characteristic absorptions at 3000–3500 cm^{-1} for overlapping ν(O–H) and ν(N–H), 1646 cm^{-1} for ν(N–C=O) amide, and 950–1250 cm^{-1} for ν(Si–O–Si) stretching vibrations.

Metal Uptake

The metal ion uptake capacity (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) as mg M^{n+}/g ligand was determined by shaking the functionalized ligand systems (P-macro) for 48 h with acetate buffer solutions at different pH values (3.5–6). The maximum metal uptake capacities versus pH are given in Fig. 1.

The results show an increase of metal ion uptake with increasing pH value and reaching its maximum nearly at pH 5.5. Lower uptake capacity occurs at lower pH values because of protonation of amine groups. Maximum metal uptake capacity by P-macro ligand system is given in

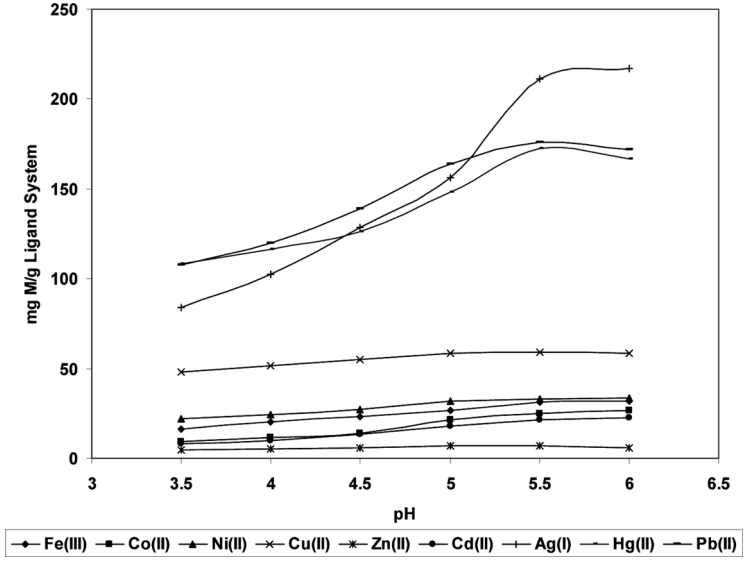


Figure 1. Metal uptake of P-macro versus pH (48 h shaking time).

Table 4. Maximum metal uptake capacity by P-macro polysiloxane ligand system

Metal ion	Maximum uptake (mg M^{n+}/g ligand)
Fe^{3+}	31.3
Co^{2+}	24.7
Ni^{2+}	32.9
Cu^{2+}	59.1
Zn^{2+}	7.2
Cd^{2+}	21.4
Ag^{+}	211.5
Hg^{2+}	172.4
Pb^{2+}	176.0

Table 4. The ligand system shows high extraction capacity for Ag^{+}, Pb^{2+}, and Hg^{2+}. It is clear that uptake of metal ions increases in the order $Ag^{+} > Pb^{2+} > Hg^{2+} > Cu^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+} > Cd^{2+} > Zn^{2+}$.

The colors of the metal ion complexes of the immobilized ligand systems are given in Table 5.

Recovery of the Ligand System from Its Metal Complexes

The recovery of metal ions after extraction by the immobilized ligand system was examined to evaluate the preconcentration and reuse efficiency of these functionalized polysiloxanes. The recovery of metal ions

Table 5. Characteristic colors of the metal complexes of P-macro polysiloxane ligand system

Metal ion	Color
Fe^{3+}	Brown
Co^{2+}	Violet
Ni^{2+}	Green
Cu^{2+}	Blue
Zn^{2+}	White
Cd^{2+}	White
Ag^{+}	Black
Hg^{2+}	Red
Pb^{2+}	Yellow

Table 6. Maximum metal uptake versus amount recovered of metal ions by EDTA

Metal	Maximum uptake (mg of metal ion/g ligand system)	Amount recovered (mg of metal ion/g ligand system)	Efficiency (%)
Fe^{3+}	31.3	15.3	49.1
Co^{2+}	24.7	20.5	82.9
Ni^{2+}	32.9	25.7	78.1
Cu^{2+}	59.06	36.0	61.0
Zn^{2+}	7.2	5.5	76.3
Cd^{2+}	21.4	12.3	57.5
Ag^{+}	211.5	3.05	1.4
Hg^{2+}	172.4	40.0	23.2
Pb^{2+}	176.0	96.7	55.0

(Cu^{2+}, Hg^{2+}, Pb^{2+}, and Ag^{+}) from their ligand complexes (at their optimum values) using an EDTA solution showed variable efficiencies. The results are given in Table 6.

It is observed that the efficiency of metal ion recovery is in the following order: $Co^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+} > Pb^{2+} > Fe^{3+} > Hg^{2+} > Ag^{+}$.

On the other hand, washing the ligand complex with HCl (1 M) removed nearly all the metal ions and produced a clean immobilized ligand system.

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